

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 094 532 A1

(12)

## EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

25.04.2001 Bulletin 2001/17

(51) Int. Cl.<sup>7</sup>: H01M 4/58, H01M 10/40,  
H01M 4/04

(21) Application number: 00911428.1

(86) International application number:  
PCT/JP00/01915

(22) Date of filing: 28.03.2000

(87) International publication number:  
WO 00/60679 (12.10.2000 Gazette 2000/41)

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE

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(30) Priority: 06.04.1999 JP 9940799

28.09.1999 JP 27474699

28.09.1999 JP 27474799

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### (54) METHOD FOR MANUFACTURING ACTIVE MATERIAL OF POSITIVE PLATE AND METHOD FOR MANUFACTURING NONAQUEOUS ELECTROLYTE SECONDARY CELL

(57) In a method for producing a positive electrode active material including a mixing step of mixing a plurality of substances to give a precursor and a sintering step of sintering and reacting said precursor obtained by said mixing step, in which these substances prove a starting material for synthesis of a compound represented by the general formula  $\text{Li}_x\text{M}_y\text{PO}_4$  where  $x$  is such that  $0 < x \leq 2$ ,  $y$  is such that  $0.8 \leq y \leq 1.2$  and  $M$  includes at least one of 3d transition metals., a reducing agent is added in the above mixing step to said precursor to render it possible to prepare a positive electrode active material capable of reversibly and satisfactorily doping/undoping lithium.

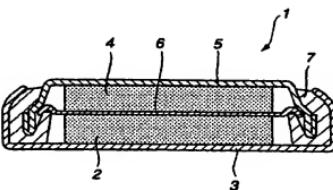


FIG.1

**Description****Technical Field**

[0001] This invention relates to a method for producing a positive electrode active material that is capable of reversibly doping/undoping lithium, and a method for producing a non-aqueous electrolyte secondary battery employing this positive electrode active material.

**Background Art**

[0002] Recently, with the marked progress in a variety of electronic equipment, researches in a rechargeable secondary battery, as a battery that can be used conveniently and economically for prolonged time, are underway. Typical of the known secondary batteries are a lead battery, an alkali storage battery and a lithium secondary battery.

[0003] Of these secondary batteries, a lithium secondary battery has advantages as to high output and high energy density. The lithium secondary battery is made up at least of positive and negative electrodes, containing active materials capable of reversibly introducing and removing lithium ions, and a non-aqueous electrolyte.

[0004] Currently, LiCoCO<sub>2</sub> is widely exploited as a positive electrode active material of a lithium ion secondary battery having a potential of 4V with respect to the lithium potential. This LiCoCO<sub>2</sub> is of a high energy density and a high voltage and is an ideal positive electrode material in many respects. However, Co is localized in distribution and represents a rare resources, with the result that, if LiCoCO<sub>2</sub> is used as a positive electrode active material, the cost is raised, whilst stable supply is difficult.

[0005] Therefore, development of a electrode active material based on Ni, Mn or Fe, that is abundant in supply and inexpensive, is desirable. For example, LiNiO<sub>2</sub>, based on Ni, has a large theoretical capacity and a high discharging potential. However, in a battery employing LiNiO<sub>2</sub>, the LiNiO<sub>2</sub> crystal structure collapses with the charging/discharging cycles, so that the discharging capacity is lowered. On the other hand, LiNiO<sub>2</sub> suffers a drawback or poor thermal stability.

[0006] As an Mn-based electrode active material, there is proposed LiMn<sub>2</sub>O<sub>4</sub> having a positive spinel structure and a spatial set Fd3m. This LiMn<sub>2</sub>O<sub>4</sub> has a high potential of the order of 4V, with respect to the lithium potential, which is equivalent to that of LiCoCO<sub>2</sub>. Moreover, the LiMn<sub>2</sub>O<sub>4</sub> is a highly promising material since it is easy to synthesize and has high battery capacity. However, the battery constructed using LiMn<sub>2</sub>O<sub>4</sub> is deteriorated in battery capacity since Mn is dissolved in the electrolytic solution with the charging/discharging cycles so that it is insufficient in stability or cycle characteristics.

[0007] On the other hand, such a material having

LiFeO<sub>2</sub> as a basic structure is being researched as an Fe-based electrode active material. Although LiFeO<sub>2</sub> has a structure similar to that of LiCoCO<sub>2</sub> or LiMn<sub>2</sub>O<sub>4</sub>, it is unstable in structure and difficult to synthesize.

[0008] On the other hand, a compound having an olivine structure as a positive electrode active material of the lithium secondary battery, such as, for example, a compound represented by the general formula Li<sub>x</sub>M<sub>y</sub>PO<sub>4</sub>, where x is such that 0 < x ≤ 2, y is such that 0.8 ≤ y ≤ 1.2 and M contains at least one of 3d transition metals (Fe, Mn, Co and Ni), is retained to be a promising material.

[0009] It is proposed in Japanese Laying-Open Patent H-9-171827 to use e.g., LiFePO<sub>4</sub>, amongst the compounds represented by the general formula Li<sub>x</sub>M<sub>y</sub>PO<sub>4</sub>, as a positive electrode of a lithium ion battery. This LiFePO<sub>4</sub> has a theoretical capacity as large as 170 mAh/g and contains one Li atom, that can be electrochemically doped/undoped in an initial state, per Fe atom, and hence is a promising material as a positive electrode active material for the lithium ion battery.

[0010] Conventionally, this LiFePO<sub>4</sub> has been synthesized by sintering at a higher temperature of 800°C, under a reducing environment, using a bivalent iron salt, such as iron phosphate Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> or iron acetate Fe(CH<sub>3</sub>COO)<sub>2</sub>, as an Fe source which proves a starting material for synthesis.

[0011] However, Fe<sup>2+</sup> is sensitive to a trace amount of oxygen contained in a synthesizing atmosphere and is readily oxidized to Fe<sup>3+</sup>. The result is that trivalent iron compounds tend to co-exist in the produced Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> to render it difficult to acquire single-phase LiFePO<sub>4</sub>.

[0012] It is reported in the above Publication that an actual battery fabricated using the Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> synthesized by the above-described synthetic method has an actual capacity only as low as approximately 60 mAh/g to 70 mAh/g. Although the actual capacity of the order of 120 mAh/g is subsequently reported in the Journal of the Electrochemical Society, 144,1188 (1997), it cannot be said that a sufficient capacity has been achieved, in consideration that the theoretical capacity is 170 mAh/g.

[0013] If LiFePO<sub>4</sub> is compared to LiMn<sub>2</sub>O<sub>4</sub>, the former has a volumetric density of 3.6 g/cm<sup>3</sup> and an average voltage of 3.4 V, whereas latter has a volumetric density of 4.2 g/cm<sup>3</sup> and an average voltage of 3.9 V, with the capacity being 120 mAh/g. So, LiFePO<sub>4</sub> is lower than LiMn<sub>2</sub>O<sub>4</sub> by approximately 10% in both the voltage and volumetric density. So, for the same capacity of 120 mAh/g, LiFePO<sub>4</sub> is lower than LiMn<sub>2</sub>O<sub>4</sub> by not less than 10% and by not less than 20% in weight energy density and in volumetric energy density, respectively. Thus, in order to realize the energy density of LiFePO<sub>4</sub> which is of the level equivalent to or higher than LiMn<sub>2</sub>O<sub>4</sub>, the capacity of 140 mAh/g or higher is required. However, this high capacity has not been realized with LiFePO<sub>4</sub>.

[0014] On the other hand, LiFePO<sub>4</sub> obtained by the conventional synthesizing method is lower in electrical